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THE PREPARATION AND STUDY OF THE PROPERTIES OF POLYMERS OF 1,1'-FERROCENEDICARBOXYLIC ACID

A Thesis

Presented to

the Faculty of the Graduate School

Appalachian State Teachers College

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

---

by

James Carson Greene

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APPROVAL SHEET

THE PREPARATION AND STUDY OF THE PROPERTIES OF POLYMERS OF 1,1'-FERROCENEDICARBOXYLIC ACID

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TABLE OF CONTENTS

CHAPTER PAGE

LIST OF FIGURES

CHAPTER I

THE PROBLEM

The purpose of this research is to (1) prepare polymers of dicyclopentadienyl iron (ferrocene) which have not been prepared, (2) to study the properties of these polymers, (3) to study the infared (I.R.) spectra of each polymer and the intermediate compounds from which it was prepared, and (4) to study the static charge properties of these polymers.

CHAPTER II

INTRODUCTION

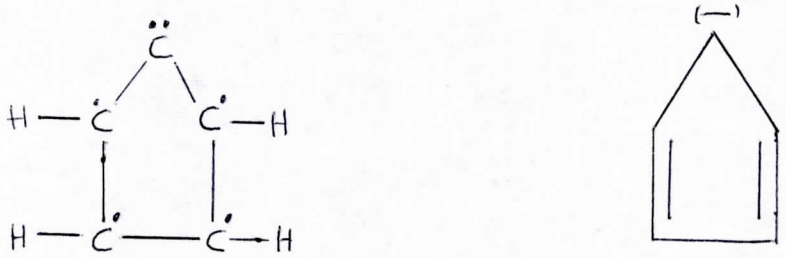
A. Properties of Ferrocene

Ferrocene was first discovered in 1951 by Kealy and Pauson.[1] X-ray data showed that the molecule had a sandwich-type structure with two cyclopentadienyl rings in parallel planes and all carbon atoms in each ring were equal distance from the center. The I. R. absorption of ferrocene in the 3-4 μ region showed a single sharp peak at 3.25 μ, this indicates the carbon-hydrogen bonds are of only one type. This absorption band is in the range observed for carbon-hydrogen stretching in benzenoid compounds.[2] The structure of ferrocene is shown in Figure 1.

Figure 1. The structure of ferrocene.

Ferrocene is a very stable compound, resisting pyrolysis in a nitrogen atmosphere up to 470° C. It is unreactive toward bases and acids in the absence of oxygen.[2] It has a resonance energy of 113 kcal./mole[3] which is higher than that for benzene, 37 kcal./mole.[4] Ferrocene will undergo electrophilic substitution but resists addition reactions.[2]

It has been shown, by Huckel, that there is a large resonance stabilization associated with a ring system with $(4n + 2)$ π electrons, where n can equal 0, 1, 2, ... Since large resonance stabilization is a characteristic of aromatic compounds, this, $(4n + 2)$ rule, is often used to indicate whether a compound is aromatic or not . The cyclopentadienyl group exists in ferrocene with 6 π electrons making it fit the $(4n + 2)$ rule where $n = 1$.



a b

Figure 2. The structure of the cyclopentadienyl group as it appears in ferrocene.

In Figure 2-a the electrons are indicated by the dots and Figure 2-b shows the structure of the cyclopentadienyl ion as it is usually drawn.

Because ferrocene obeys the $(4n + 2)$ rule, has a high resonance energy, and undergoes electrophilic substitution only; it is classified as an aromatic compound.

B. Derivatives of Ferrocene

There are two major types of ferrocene derivatives, the mono- and di- substituted compounds. Distinguishing between these two types of derivatives is done by noting the appearance or disappearance of two absorption peaks in the I.R. spectra of the compound.[5] If the derivative is disubstituted the absorption bands at 9.95 and 9.00 μ disappear; they are present in the monosubstituted derivatives.[6]

The dicarboxylic acid derivative of ferrocene exhibits the following ionization constants (K):

$$K_1 = 3.1 \times 10^{-7}$$

$$K_2 = 2.7 \times 10^{-8}.$$

The ionization constant of benzoic acid is

$$K = 2.4 \times 10^{-7}.$$

The small difference between K_1 and K_2 indicates the carboxylic groups interact very little and are far apart. Since the K_1 value of

ferrocene is near that of benzoic acid, this would indicate the ring carbon atoms of ferrocene and the central iron atom are electrically neutral, and that no form of hybridization leading to a charge separation occurs within the molecule; this lack of hybridization is also indicated by the lack of a dipole moment.[7]

All evidence indicates ferrocene has the electrons which bond the iron to the rings spread over the entire molecule, this would also be true of a ferrocene unit if it were incorporated into a polymer chain. A polymer with this type of delocalized charge should show little tendency to build up static charges.

C. Polymers

In order to prepare a polymer of ferrocene a difunctional derivative must be prepared and condensed to give a polymeric material in which the ring system would be a part of the main polymer chain. Many polymers of ferrocene have been prepared, but only those prepared from 1,1'-ferrocenedicarboxylic acid will be considered here as this was the derivative used in this study.

Polyamides and polyesters prepared from 1,1'-ferrocenedicarbonyl chloride were first reported by Knobloch and Rauscher in 1961.[8] From their study of the I.R. spectra of these polymers, they reported only the carbonyl absorption band for polyamides and polyesters

occurring at 6.1 to 6.2 μ, and 5.7 to 5.8 μ respectively. The spectra were not reproduced in the article.

In one of the polyamides prepared, hexamethylenediamine was the amine monomer. It was noted that the polymer was a yellow-orange powder that softened at 110°C, was gummy at 165°C, and turned brown slowly as the temperature approached 220°C. It was found to be soluble in m-cresol, 90% formic acid, and dimethylformamide (DMF).[8]

Hydroquinone was the phenolic monomer used in preparing one polyester. The insoluble polyester was a brown powder which darkened above 200°C with no melting point.[8]

Other polymers prepared by Knobloch and Rauscher were polyamides made from ethylenodiamine, piperazine, and p-phenylenediamine; and polyesters made from 4,4'-isopropylidenediphenol.

CHAPTER III

EXPERIMENTAL

The preparation of each intermediate ferrocene compound, the preparation of the polymers, and the procedures used to determine the properties of each are given in this section.

A. Preparation of Cyclopentadiene

Dicyclopentadiene was distilled to yield cyclopentadiene. The distillation apparatus used consisted of a 500 ml. round bottomed flask, distillation column packed with small glass spheres to a height of 10 inches, a condenser, an adaptor, and a thermometer.

Into the flask was added 100 ml. of dicyclopentadiene, Eastman technical grade, and this was heated to a gentle boil; the cyclopentadiene distilled at 39-40°C.

Most references indicate that merely "heating dicyclopentadiene at the boiling point" would yield cyclopentadiene.[9] It was found that this procedure would not give satisfactory results. Satisfactory yields of cyclopentadiene were obtained by fractional distillation only when a packed distillation column was used.

B. Preparation of Ferrocene

Ferrocene was prepared by the method used by Wilkinson.[10] Fifty-one grams of ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) was placed in a 500 ml. filter flask. The flask was heated by a Fisher burner under reduced pressure and a nitrogen atmosphere until the compound was dehydrated. The yield was 33 g. (0.25 mole) of ferrous chloride ($FeCl_2$). The $FeCl_2$ was cooled in an ice bath and added to a mixture of 42 ml. (0.5 mole) of freshly distilled cyclopentadiene and 100 ml. (0.97 mole) of diethylamine, and stirred eight hours at room temperature. The amine was removed under reduced pressure and the residue was extracted repeatedly with boiling ligroin, and filtered hot. The solvent was evaporated leaving ferrocene which was recrystallized from pentane yielding 15.2 g. (61%) which melted at 172-173°C.

Several attempts were made to prepare ferrocene by other methods such as the method of Barusch and Lindstrom[11], which consisted of adding sodium to cyclopentadiene and then adding $FeCl_2$ to this solution. Very poor results were obtained. Repeated attempts to prepare ferrocene without a completely inert atmosphere were unsuccessful. Most of the ferrocene used in this study was Eastman technical grade material.

C. Preparation of 1,1'-Diacetylferrocene

The 1,1'-diacetylferrocene derivative was prepared using a Friedel-Crafts reaction. A mixture of 80 g. (0.60 mole) of anhydrous aluminum chloride and 42.5 ml. (0.60 mole) of acetyl chloride was placed in a 500 ml., 3-necked flask equipped with a stirrer, reflux condenser, and addition funnel. A solution of 50 g. (0.28 mole) of ferrocene in 250 ml. of carbon disulfide was added dropwise over a period of 1 hour. A nitrogen atmosphere and stirring were maintained throughout the reaction. After 36 to 70 hours of stirring the hydrogen chloride evolution had ceased and the reaction mixture was hydrolyzed by adding 200 g. of ice, the mixture was filtered; the crude diacetylferrocene product was washed with water and recrystallized from 70% methanol.[12] The yield was 42 g. (58%) of red crystals with a melting point of 129-130°C. The I.R. spectra showed no absorption peaks at 9.00 and 9.95 μ, indicating the product was disubstituted.

D. Preparation of 1,1'-Ferrocenedicarboxylic Acid

In a 1-l round bottomed flask, 83 g. of commercial calcium hypochlorite was dissolved in 330 ml. of warm water, and a warm solution of 58g. of potassium carbonate and 17 g. of potassium hydroxide in 170 ml. of water was added.

The flask was stoppered and shaken vigorously; the solid was removed by filtration. The solid was washed with 70 ml. of water and sucked as dry as possible. The filtrate 500 ml., contained about 10% potassium hypochlorite.[13]

To a 500 ml. round bottomed flask equipped with a stirrer were added 26.5 g. (0.01 mole) of 1,1'-diacetylferrocene and 250 ml. of the above 10% potassium hypochlorite solution. A temperature between 40 and 50°C and stirring were maintained throughout the reaction. Additions of 100 ml. of potassium hypochlorite solution were made after 1.5, 2, and 3 hours. After the final addition the reaction mixture was stirred for 2 hours and filtered while warm. The orange filtrate was treated with aqueous bisulfite to destroy the excess hypochlorite and acidified with dilute hydrochloric acid to yield 22.3 g. of the crude acid.[8] No suitable method of recrystallization was found. Solutions of the acid degrade very rapidly. The calculated neutralization equivalent was 137; the neutralization equivalent determined experimentally was 144.

E. Preparation of 1,1'-Ferrocenedicarboxyl Chloride

To a mixture of 3 g. (0.0091 mole) of 1,1'-ferrocenedicarboxylic acid and 50 ml. of benzine was added 5 g. (0.024 mole) of phosphorus pentachloride.[14] The mixture was stirred for 2 hours under a nitrogen

atmosphere and then was evaporated to dryness under reduced pressure. The residue was extracted repeatedly with benzine,[8] yielding, after recrystallization from benzine 1.6 g. (47%) of 1,1'-ferrocenedicarbonyl chloride which melted at 97-98°C.

F. Preparation of the Polymers

All of the polymers were made using a similar procedure.

1. Preparation Of Resorcinol-Ferrocenedicarboxylic Acid Polymer

An aqueous solution containing 0.4 g. (0.0036 mole) of resorcinol, 0.3 g. (0.0075 mole) of sodium hydroxide and 50 ml. or water was stirred and added to a Waring blendor. To this was added 1 g. (0.0032 mole) of 1,1'-ferrocenedicarbonyl chloride dissolved in 25 ml. of benzine. The two solutions were mixed for 3 minutes and the dark brown polymer was filtered and dried for 12 hours at room temperature. Care must be taken not to stir the resorcinol, sodium hydroxide, and water solution too vigorously; no reaction was obtained when stirred in the Waring blendor before addition of the dichloride. The best results were obtained when an aqueous solution of sodium hydroxide was added, just before the addition of 1,1'-ferrocenedicarbonyl chloride. This was also true for the cathecol-ferrocenedicarboxylic acid polymer.

The polymer was insoluble in m-cresol; 90% formic acid; dimethylformamide; chloroform; 1,1,2,2,-tetrachloroethane; pyridine; 1,4-dioxane; and acetone. The yield was 0.68 g. (51%).

2. Preparation of Cathecol-Ferrocenedicarboxylic Acid Polymer

An aqueous solution containing 0.4 g. (0.0036 mole) of cathecol, 0.3 g. (0.0075 mole) of sodium hydroxide and 50 ml. of water was stirred and added to a Waring blendor. To this was added 1 g. (0.0032 mole) of 1,1'-ferrocenedicarbonyl chloride dissolved in 25 ml. of benzine. The two solutions were mixed for 3 minutes and the black polymer was filtered and dried for 12 hours at room temperature. The polymer was slightly soluble in dimethylformamide but insoluble in m-cresol; 90% formic acid; chloroform; 1,1,2,2,-tetrachlorethane; pyridine; 1,4-dioxane; and acetone. The yield was 1.20 g. (88%) of the polymer.

3. Preparation of Hydroquinone-Ferrocenedicarboxylic Acid Polymer

An aqueous solution containing 0.4 g. (0.0036 mole) of hydroquinone, 0.3 g. (0.0075 mole) of sodium hydroxide and 50 ml. of water was stirred and added to a Waring blendor. To this was added 1 g. (0.0032 mole) of 1,1'-ferrocenedicarbonyl chloride dissolved in 15 ml. of benzine. The two solutions were mixed for 3 minutes and the dark brown polymer was filtered and dried for 12 hours at room temperature. The polymer was insoluble in dimethylformamide; m-cresol; 90%

formic acid; chloroform; 1,1,2,2,-tetrachloroethane; pyridine; 1,4-dioxane; and acetone. The yield was 0.80 g. (60%).

These results are similar to those obtained by Knobloch and Rauscher.[8] They found the polymer insoluble, obtained a 63% yield, and observed the same melting point that was noted in this research. (See Table I).

4. Preparation of Hexamethylenediamine-Ferrocenedicarboxylic Acid Polymer

An aqueous solution containing 0.4 g. (0.0034 mole) of hexamethylenediamine, 0.3 g. (0.0075 mole) of sodium hydroxide and 50 ml of water was stirred and added to a Waring blendor. To this was added 1 g. (0.0032 mole) of 1,1'-ferrocenedicarbonyl chloride dissolved in 25 ml. of benzine. The two solutions were mixed for 3 minutes and the brown polymer was filtered and dried for 24 hours at room temperature. The polymer was slightly soluble in dimethylformamide but insoluble in m-cresol; 90% formic acid; chloroform; 1,1,2,2,-tetrachloroethane; pyridine; 1,4-dioxane; and acetone. The yield was 0.82 g. (60%). This polymer gradually decomposed from 250° C. to 300° C.

When the hexamethylenediamine, sodium hydroxide, and water were stirred in the Waring blendor and the 1,1'-ferrocenedicarbonyl chloride was added to this mixture, a tan polymer was the product;

the yield was 1.12 g. (82%). This polymer softened at 120° C. and decomposed between 200° and 250° C. It was soluble in dimethyl formamid, m-cresol, and 90% formic acid. The properties of this tan hexamethylenediamine-ferrocenedicarboxylic acid polymer were very similar to the properties obtained by Knobloch and Rauscher.[8]

G. Preparation of Polyamide Films

Films of the hexamethylenediamine polymer were cast from dimethylformamide. Approximately 1 g. of polymer was dissolved in 25 ml. of DMF and approximately 5 ml. of the solution was deposited evenly on a 4 in. by 4 in. glass plate and allowed to evaporate at room temperature. This procedure was repeated until the film was thick enough to peal off the plate. The brittle dark red film was separated from the plate by the use of a razor blade.

H. Preparation of Potassium Bromide Pellets

The potassium bromide (KBr) pellets were prepared by grinding approximately 1 mg. of the sample with 100 mg. of dried KBr. Each pellet was pressed under a vacuum with a perssure of 3,500 psi for 15 minutes. The pellet was then removed and stored in a desiccator.

I. Procedure For Obtaining The I.R. Spectra

The Perkin-Elmer 137 Infracord Spectrophotometer was used for determining all the I.R. spectra. The instrument was allowed to warm up for 1 hour. All the spectra were run at a slit width setting of 25 . After the 100% transmittance was set, the sample was placed in the sample holder and the spectrum was recorded using the slow scanning speed. An I.R. spectrum was determined for each of the intermediates (except 1,1'-ferrocenedicarbonyl chloride) and the polymers.

J. Procedure For Determining Solubilities

The solubilities were determined by placing approximately 50 mg. of the polymer in 10 ml. of the solvent and observing for 24 hours at room temperature. The solvents used were m-cresol; 90% formic acid; dimethylformamide; chloroform; 1,1,2,2,-tetrachloroethane; pyridine; 1,4-dioxane; and acetone.

K. Procedure For Determining Neutralization Equivalents

The neutralization equivalent was determined by adding 35 ml. of 0.1124 N. sodium hydroxide to 0.5002 g. of 1,1'-ferrocenedicarboxylic acid and back-titrating with 4.31 ml. of 0.1090 N.

hydrochloric acid. The end-point was found using a Fisher titrimeter. The instrument was calibrated with an acetate buffer with a pH of 6.85.

CHAPTER IV

RESULTS AND DISCUSSION

Two new polymers were made and their physical properties and I.R. spectra were studied. Attempts to determine the static charges of the polymers were unsuccessful.

A. Physical Properties Of The Polymers

The polyesters prepared from resorcinol and cathecol had not been reported before; the polyester prepared from hydroquinone and the polyamide prepared from hexamethylenediamine had been reported by Knobloch and Rauscher.[8] A summary of the physical properties and the reaction conditions for the preparation of these polymers are given in Table I.

B. Infared Spectral Data

The I.R. spectra of each compound was taken from a pellet composed of KBr and the sample. The spectra of ferrocene, 1,1'-ferrocenedicarboxylic acid and each polymer are found in Figures 3 through 9.

The I.R. spectrum of a film of hexamethylenediamine polymer

TABLE I

POLYMERS PREPARED FROM 1,1'-FERROCENEDICARBONYL CHLORIDE

Monomer	Base	Reaction Time	Yield	Physical State and Melting	Solubility
	Polyesters				
Resorcinol	NaOH	3 Min.	51%	Dark brown; powder; soften 120°C; decomposes 200-220°C.	Insol.
Cathecol	NaOH	3 Min.	88%	Black powder; slowly decomposes above 250°C.	Slightly sol. DMF
Hydroquinone	NaOH	3 Min.	60%	Dark brown; powder; soften 150°C; decomposes above 200°C.	Insol.
	Polyamides				
Hexamethylenediamine	NaOH	3 Min.	60%	Dark brown; powder; gradually decomposes above 250°C.	Slightly sol. DMF
	NaOH	3 Min.	82%	Tan powder; decomposes from 200-250°C.	Sol. DMF, M-cresol, and 90% Formic Acid

was compared with the spectrum taken from a KBr pellet. The major difference between the two spectra was in the sharpness and depth of the peaks. (See Figures 4 and 5.)

The spectra of each polymer is compared to the spectra of 1,1'-ferrocenedicarboxylic acid. (Figure 6)

1. Infared Spectrum Of Hexamethylenediamine Polymer

In the spectrum of the hexamethylenediamine polymer, Figure 4, peaks at 5.9 μ that were due to carboxylic groups, disappeared and peaks at 3.4, 6.0, and 7.7 μ, due to amide linkages, appeared.

2. Infared Spectrum Of Resorcinol Polymer

The spectrum of the resorcinol polymer, Figure 7, showed peaks at 2.9, 6.2, and 8.8 μ ; these were due to hydroxy groups. Carboxylic absorption peaks disappeared at 3.4 and 7.1 μ but were retained at 6.0 and 7.5 μ.

3. Infared Spectrum Of Cathecol Polymer

The spectrum of the polyester prepared from cathecol, Figure 8, showed peaks due to hydroxy groups at 2.8 and 8.2 μ. The carboxylic absorption peaks appeared at 6.65 and 7.9 μ ; the others, at 5.7 and 7.1 μ disappeared.

4. Infared Spectrum Of Hydroquinone Polymer

The hydroquinone polyester spectrum, Figure 9, was different

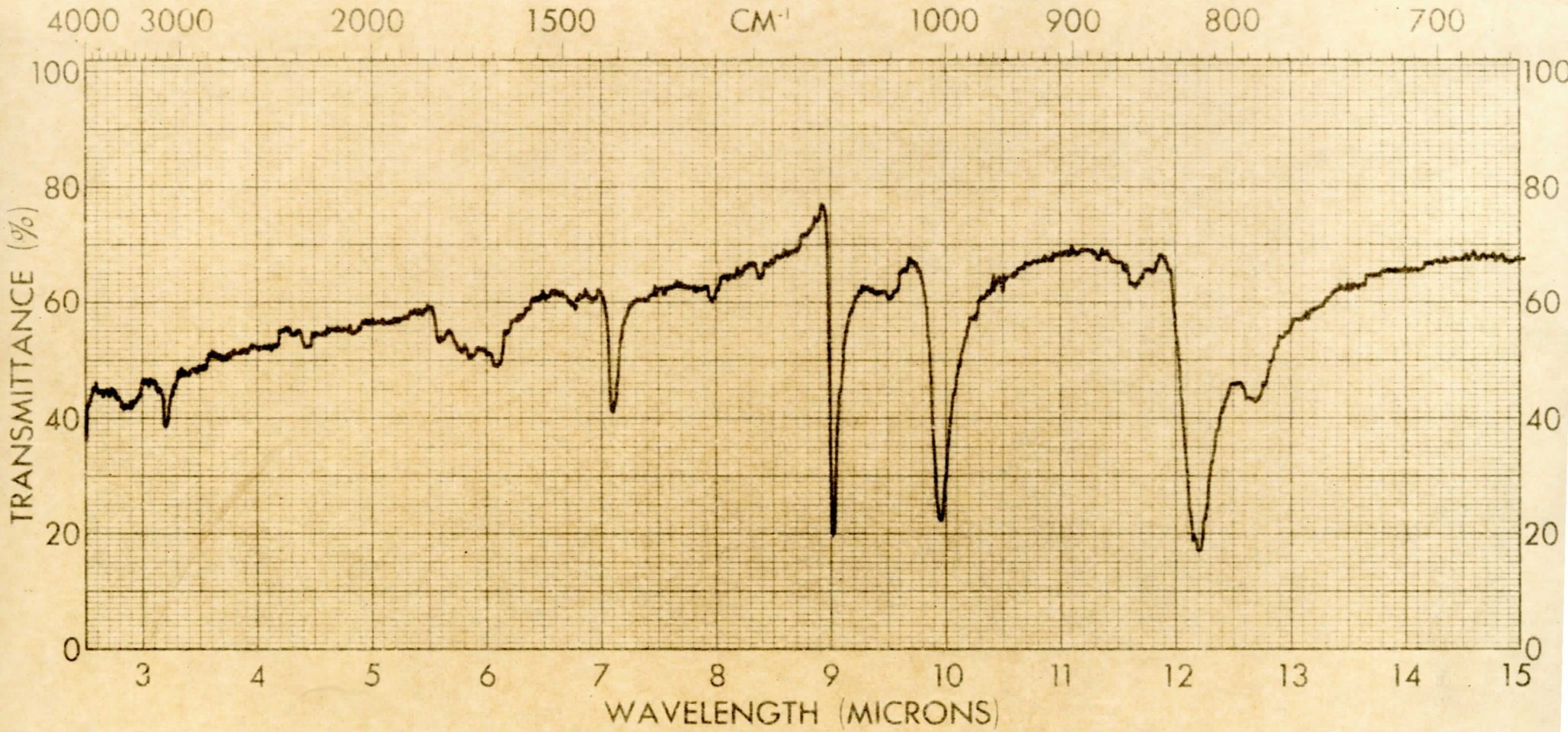


FIGURE 3

SPECTRUM OF FERROCENE

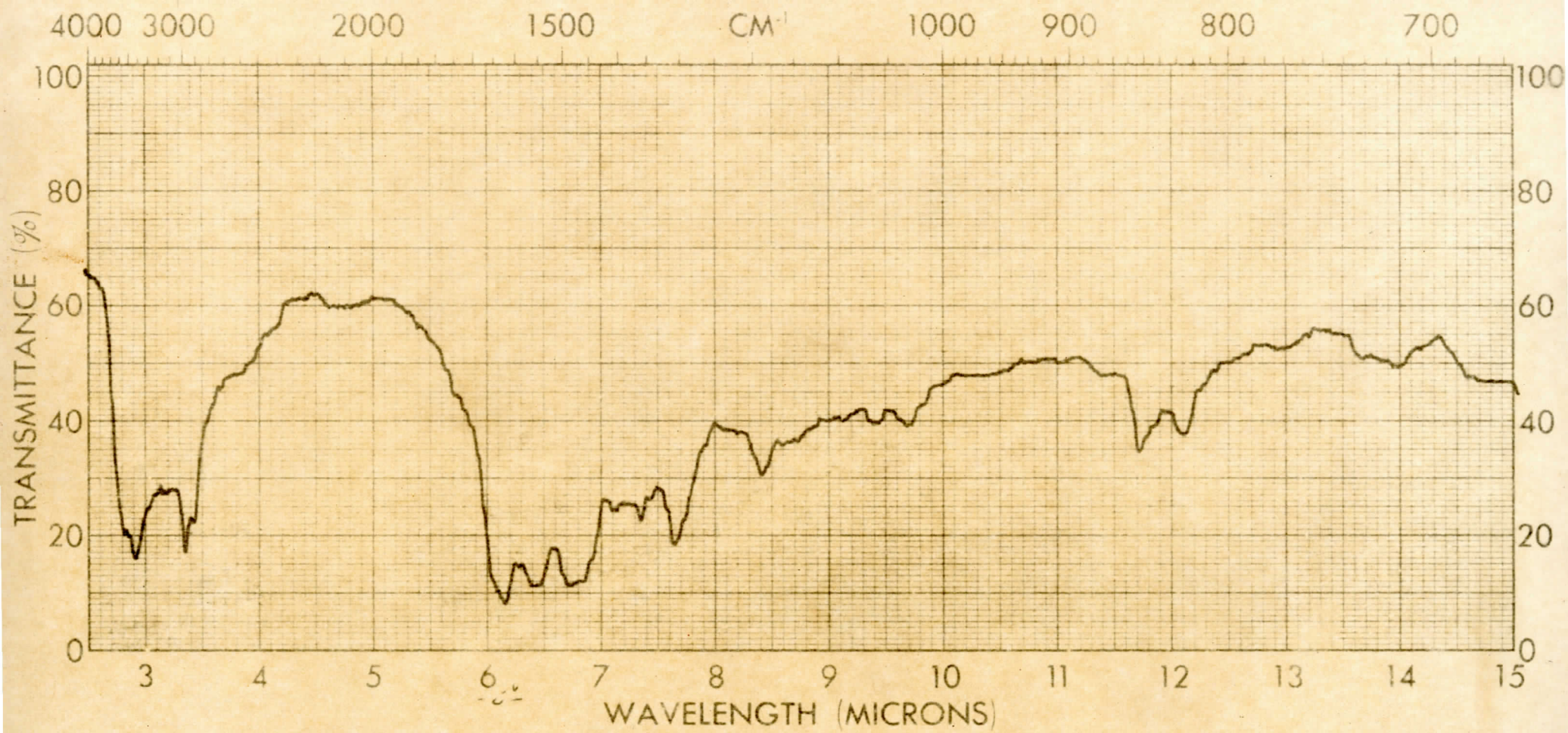


FIGURE 4

SPECTRUM OF HEXAMETHYLENEDIAMINE POLYMER

USING THE KBr PELLET METHOD

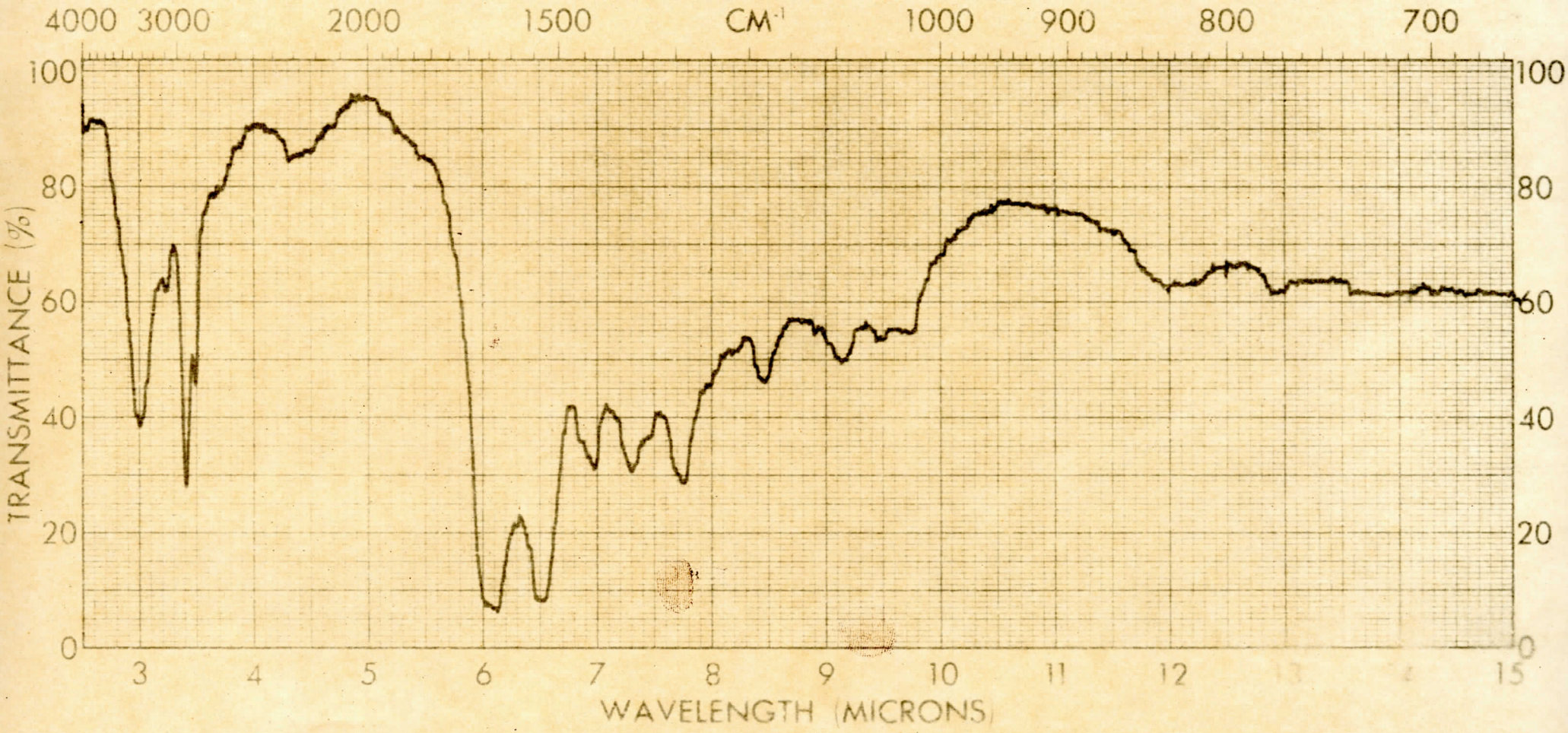


FIGURE 5

SPECTRUM OF HEXAMETHYLENEDIAMINE POLYMER (FILM)

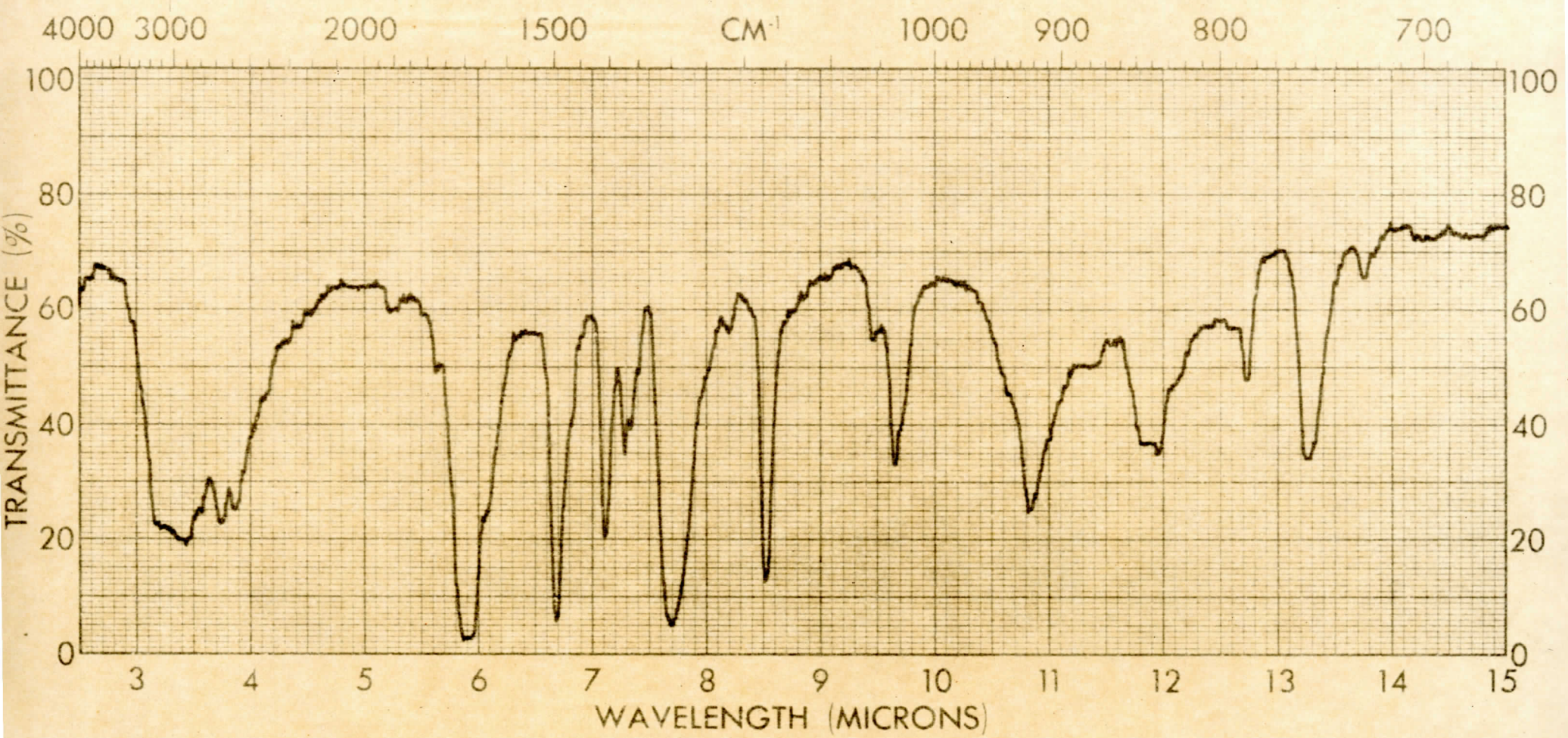


FIGURE 6

SPECTRUM OF 1,1'-FERROCENEDICARBOXYLIC ACID

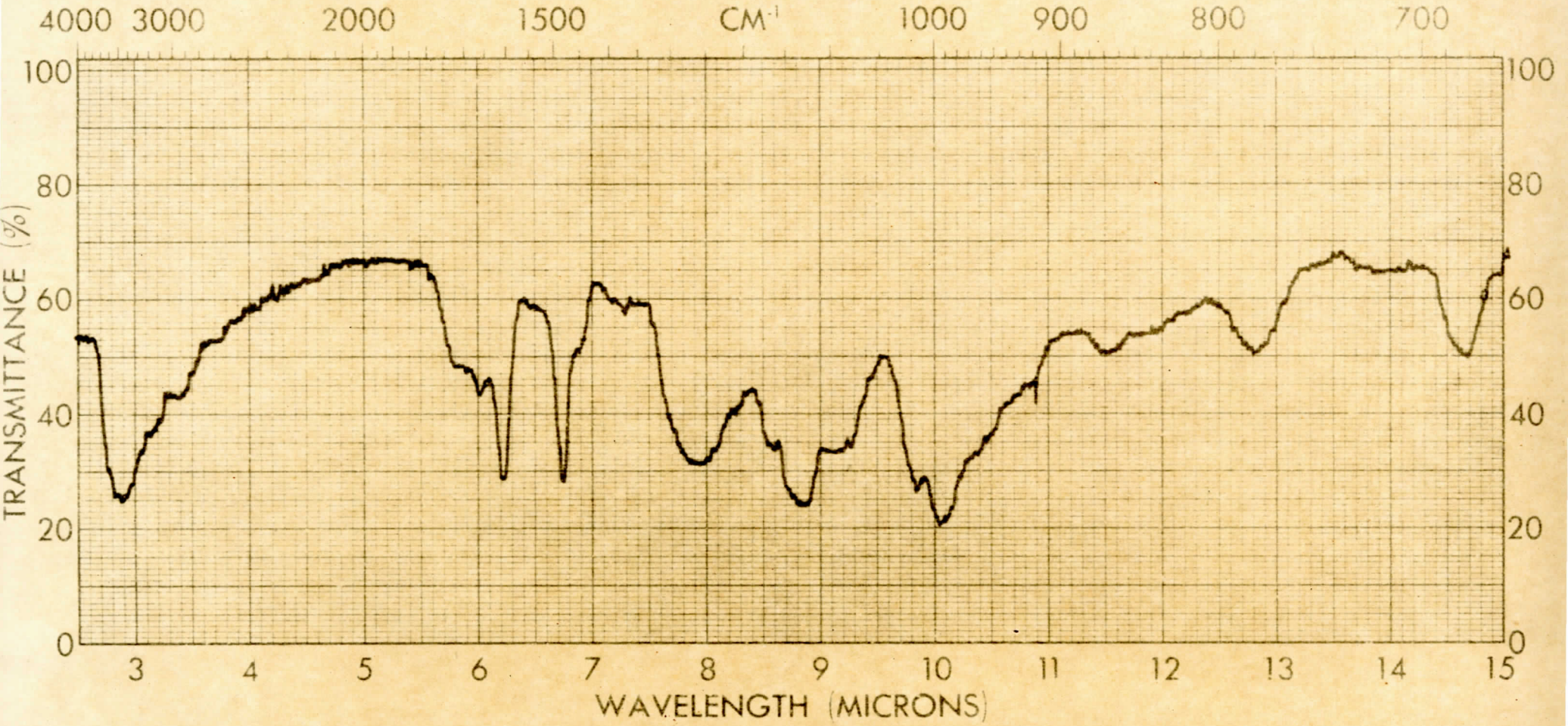


FIGURE 7

SPECTRUM OF RESORCINOL POLYMER

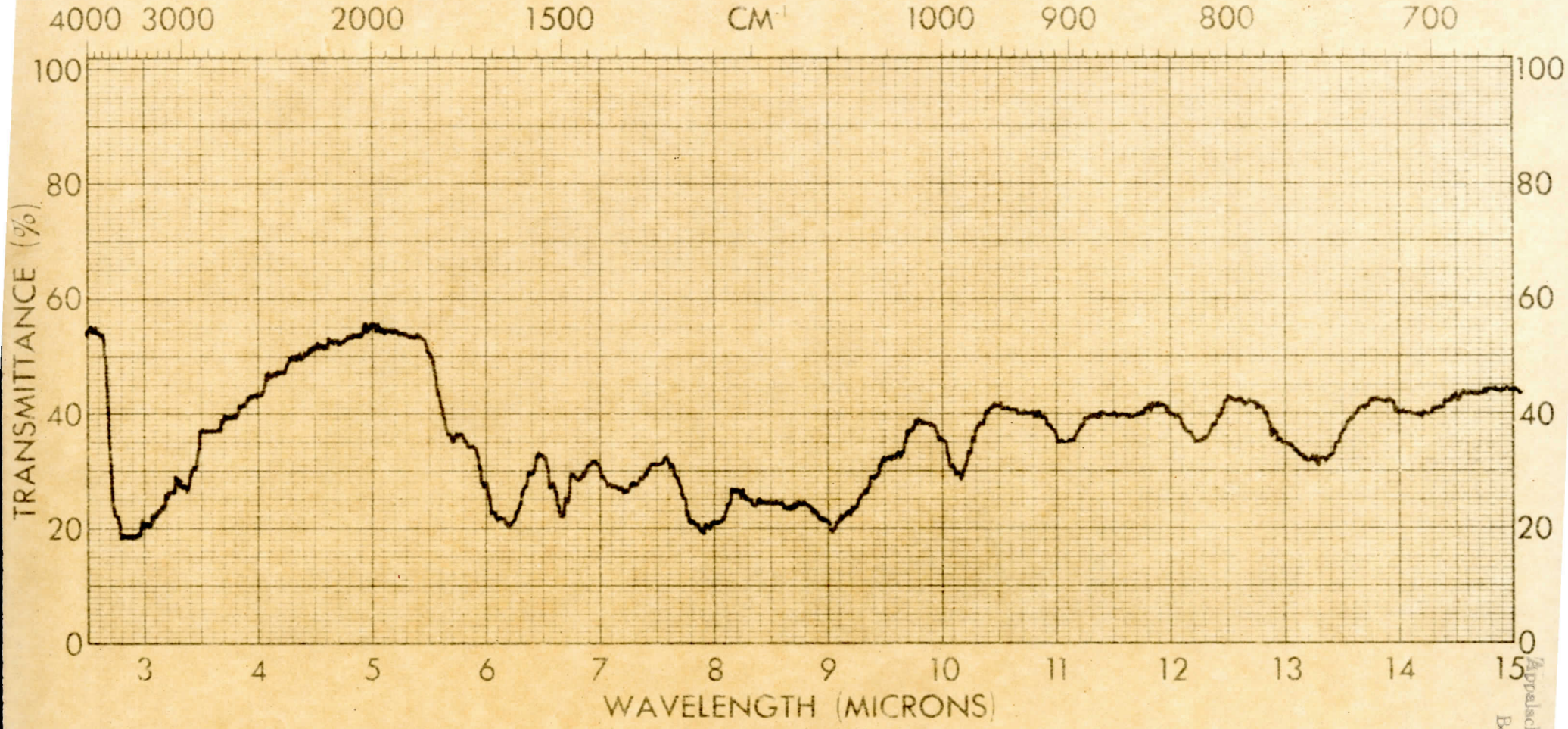


FIGURE 8

SPECTRUM OF CATHECOL POLYMER

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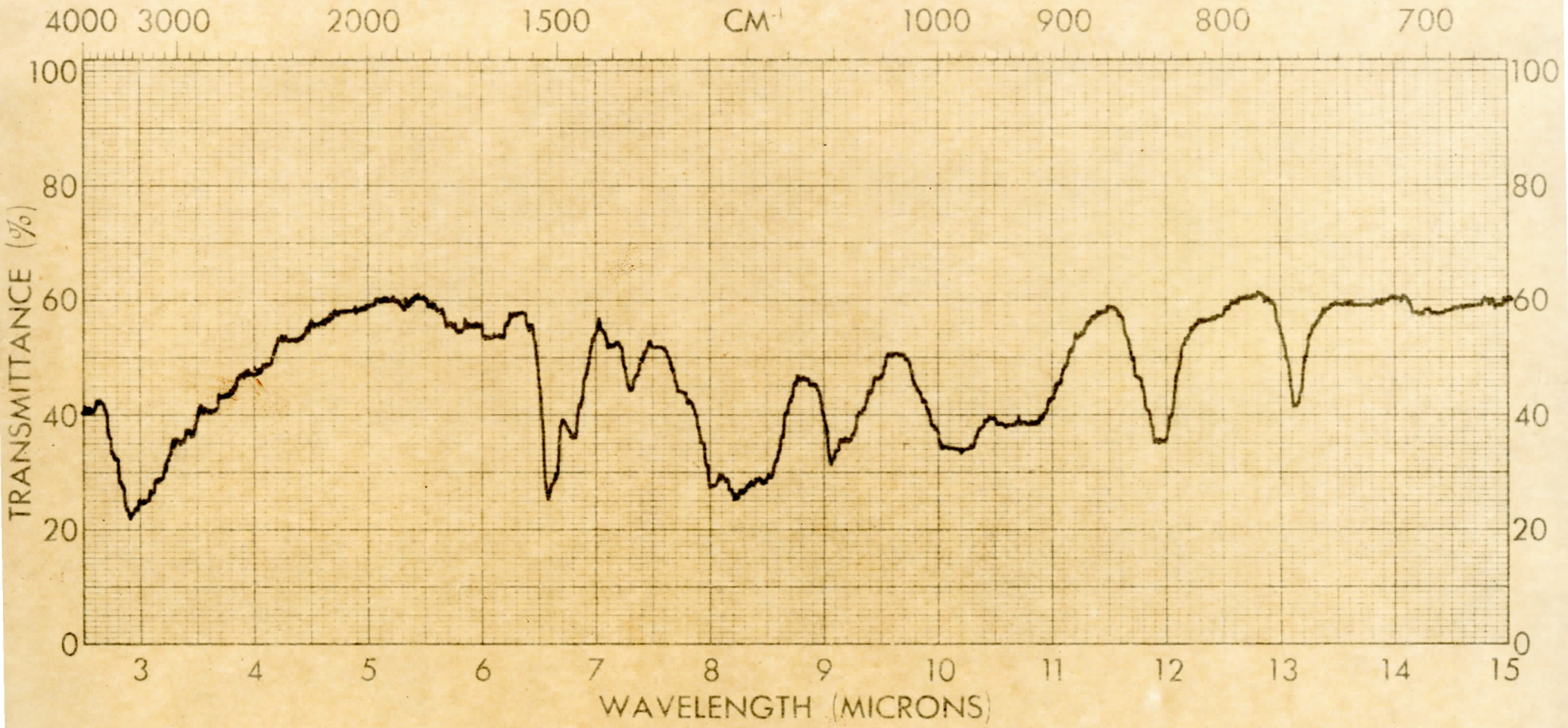

FIGURE 9

SPECTRUM OF HYDROQUINONE POLYMER

from the other polyesters in that the peaks due to the hydroxy linkages appeared at 7.3 and 9.1 μ in addition to the bands at 2.8 and 8.2 μ. The carboxylic groups appeared at 6.6 μ only, and disappeared at 3.4, 5.5, 7.1, and 7.7 μ.

C. Static Charge Properties

In order to study the static properties of the polymers a plyable polymer is needed. All the ferrocene polymers that were made appeared crystalline, and the one film made from the polyamide was very brittle, therefore this part of the research was abandoned.

CHAPTER V

SUMMARY

Ferrocene is a very stable, aromatic compound which has a delocalized charge. Polymers of ferrocene were made by polymerizing 1,1'-ferrocenedicarbonyl chloride with difunctional phenols and amines. The properties of these polymers were studied.

Ferrocene, prepared by the reaction of $FeCl_2$ with cyclopentadiene in diethylamine, was acetylated using the Friedel-Crafts reaction. The 1,1'-diacetylferrocene compound was oxidized to the acid, and the acid converted to the dicarbonyl chloride with phosphorous pentachloride. 1,1'-Ferrocenedicarbonyl chloride was polymerized with hexamethylenediamine, hydroquinone, resorcinol, and cathecol.

The polyesters prepared from resorcinol and cathecol have not been reported before. Both are largely insoluble, dark in color, and decompose above 200° C.

The I.R. spectra indicated a reaction had occurred by the appearance of absorption peaks due to hydroxyl groups and the disappearance of some of the carboxylic group peaks.

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